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PMO THEORY FOR HYDROGEN ABSTRACTION FROM SATURATED HYDROCARBONS

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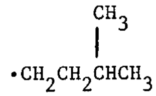
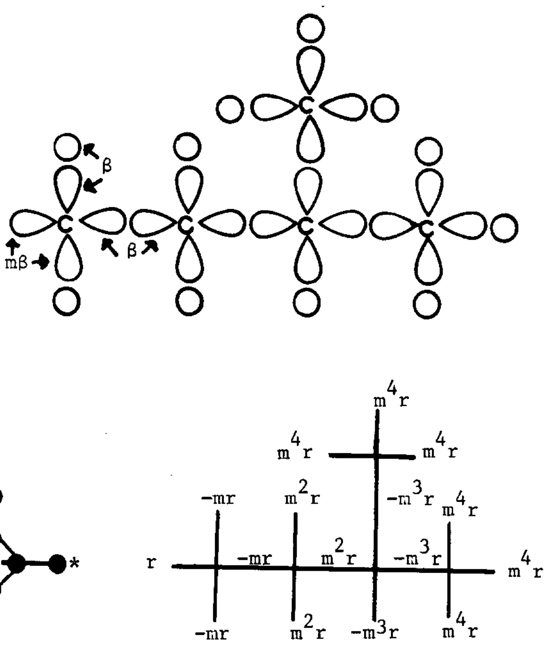
Summary. Saturated hydrocarbon radicals in the hybrid orbital all-valence-electron basis possess a nonbonding molecular orbital whose eigencoefficients can be written by inspection. Perturbational MO calculations using these coefficients lead to good correlations of hydrogen abstraction reactivity data.

Fukui and coworkers have developed a valence-electron Hückel-type molecular orbital treatment of saturated organic molecules and radicals.[1] Reactivity indices like frontier electron densities and delocalizabilities[2-4] correlate with activation energies for hydrogen abstraction by halogen atoms, CH_3 radicals, or CF_3 radicals.[5] Brown used a bond-orbitals molecular orbital method to calculate energy differences between alkanes and corresponding radicals,[6] and a similar correlation of free radical reactivity data is obtained. In a recent communication by Boldt and coworkers,[7] delocalizabilities calculated with MINDO/3 data are also shown to correlate with activation energies for CF_3 and CH_3 radical abstraction reactions.[8] These treatments all require the use of highly parameterized molecular orbital methods and computers to carry out the calculations. In the work reported here I demonstrate that the same high degrees of correlation can be obtained quickly by hand using a non-bonding molecular orbital (NBMO) perturbation theory approach.

Saturated hydrocarbon radicals can be described as linear combinations of carbon sp^3 hybrid orbitals and hydrogen 1s orbitals, as shown in 1 for isopentanyl radical. One hybrid orbital does not participate in covalent bonding. Based on previous work,[9,10] the Coubomb integrals of these basis sp^3 and 1s orbitals can be considered to have equal numerical values.[11] To a good approximation exchange intergrals for $C(sp^3)-C(sp^3)$ and $C(sp^3)-H(1s)$ bonds can also be chosen to be equal.[11] The only remaining parameter required to allow MO calculations is the relative value (m) of the exchange integral between $C(sp^3)$ hybrid orbitals of the same carbon atom. Excellent quantitative results have been obtained for many kinds of calculated physical and chemical properties using m^2=0.126.[1-4,9,12]



$\cdot CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3$



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Each sigma orbital system can be represented by a molecular graph whose connectivity is isomorphic with that of the orbital system. The vertices of the graph represent orbitals, and the lines stand for orbital interactions. The graph of the orbital system is not alternant, but it is starable in such a way that the number of starred positions exceeds unstarred positions by unity, and no starred positions in the molecular graph are adjacent. These conditions satisfy the criteria[12] for the existence of a single NBMO in an electronic system that consists of an odd number of isoenergetic basis orbitals.[14]

The coefficients of the NBMO are non-zero only at the starred orbital positions and they can be written by inspection. Examination of the secular equations[9] shows that they follow the regular pattern starting from the unpaired orbital center, r, $-mr$, $+m^2r$, $-m^3r$, etc. If $m = 1$, this would be the familiar pattern for NBMO's in π systems. The magnitude of r is determined by the normalization requirement. One can see that the odd electron is delocalized, but the odd electron density is rapidly damped with increasing distance from the radical center.

Column 2 of Table I gives r for several alkyl radicals. The r values decrease in the order CH_3, primary, secondary, tertiary, which is the correct qualitative order of hydrogen abstraction reactivity in free radical reactions. More significantly, first-order perturbation (PMO) theory quantitatively relates r to the strength of the partial bond from hydrogen atom to alkyl residue in the transition state for hydrogen atom abstraction. The larger is r, the larger should be the Arrhenius activation energy, and the relationship should be linear. A very wide range of reactivities is encompassed by such a relationship as demonstrated by the

Table I. Arrhenius Activation Energies[a] and NBMO Coefficients

For Hydrogen Abstraction from Alkanes by Radicals

alkyl radical	NBMO coefficient r		Activation Energies (kJ/mole)			
			Cl	CF_3	CH_3	Br
CH_3	0.852	$(1+3m^2)^{-1/2}$	16.0	47.0	60.9	76.1
CH_3CH_2	0.838	$(1+3m^2+3m^4)^{-1/2}$	4.3	35.3	50.0	55.2
$CH_3(CH_2)_2$	0.836	$(1+3m^2+3m^4+3m^6)^{-1/2}$	4.1		48.7	
$CH_3(CH_2)_3$	0.836	$(1+3m^2+3m^4+3m^6+3m^8)^{-1/2}$	3.2		49.1	
$(CH_3)_3CCH_2$	0.833	$(1+3m^2+3m^4+9m^6)^{-1/2}$	3.8	35.2	50.4	58.9
$(CH_3)_2CH$	0.824	$(1+3m^2+6m^4)^{-1/2}$	2.8	26.9	43.3	41.6
$CH_3CH_2(CH_3)CH$	0.822	$(1+3m^2+6m^4+3m^6)^{-1/2}$	1.3	23.9	40.7	42.0
$(CH_3)_3C$	0.811	$(1+3m^2+9m^4)^{-1/2}$	0.4	19.7	34.4	31.4
	correlation coeff.	$(\Delta E,r)$	0.945[b]	0.988	0.988	0.979

[a] As cited in ref. 5, pp. 175, 241. Also see Trotman-Dickenson, A. F. Adv. in free Radical Chem., **1**, 38 (1965). [b] CH_3. value omitted, see text.

remaining data in Table I. The only deviation from linear relationships is found in the chlorine atom data where a plot of r versus activation energy is distinctly curved, and the methyl hydrogen abstraction activation energy seems higher than would be expected. This anomaly may point to a limitation of this NBMO-PMO approach.

The correlations in Table I are not surprising. The NBMO coefficients have previously been shown to correlate precisely with CH and CC bond dissociation energies,[10] which in turn are well-known to correlate with reaction enthalpies or activation energies in these free radical reactions.[15,16] There are two unique advantages of the NBMO-PMO theoretical treatment of saturated systems. First, calculations can be carried out in a few seconds, allowing numerous applications with little labor. Second, no extensive parameterization is needed to yield results that are consonant with experimental data. Further development of this method and applications to other types of reactivity data are in progress.

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(11) Coulomb integrals can be chosen as the negative of valence-state ionization potentials, giving $\alpha(H) = 13.60$ eV and $\alpha(sp^3) = 13.96$ eV. The ratio of the resonance integrals for CH and CC bonds is 1.04 from overlap integrals or 1.17 from the ratio of average bond strengths. Neither approximation, $\alpha(H) = \alpha(sp^3)$ or $B(CH) = B(CC)$, is unreasonable. For a more detailed discussion see J. A. Pople and D. P. Santry, Mol. Physics, 7, 269 (1964); ibid, 9, 301 (1965).

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